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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US96/20267 <b>(22) International Filing Date:</b> 18 December 1996 (18.12.96)  <b>(30) Priority Data:</b> 08/575,161 19 December 1995 (19.12.95) US  <b>(71) Applicant:</b> TALISON RESEARCH [US/US]; Suite 210, 1250 Oakmead Parkway, Sunnyvale, CA 94086-4027 (US).  <b>(72) Inventors:</b> KOLLURI, Omprakash, S.; 2305 Cervantes Way, Campbell, CA 95008 (US). JOHANSON, Robert, G.; 517 Kenilworth Court, Sunnyvale, CA 94087 (US).  <b>(74) Agent:</b> FRANCIS, Ralph, C.; Francis Law Group, Suite 901, 1901 Harrison Street, Oakland, CA 94612 (US).		<b>(81) Designated States:</b> CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PLASMA DEPOSITED FILM NETWORKS  <b>(57) Abstract</b>  A three-dimensional functional film network comprising a plurality of radio frequency discharge plasma film layers. The plasma film layers include a first layer, comprising a plurality of a first functional group, and a second layer, comprising a plurality of a second functional group. The employment of three-dimensional film networks with desired functional groups located either on the periphery or both the periphery and interstitial spaces of the networks significantly increases the surface functional density.		

## PLASMA DEPOSITED FILM NETWORKS

### BACKGROUND OF THE INVENTION

#### 5 Field of the Invention

The present invention relates to functional film networks, and in particular to sequentially deposited radio frequency plasma film layers having an open network structure, thereby increasing interstitial spacing between plasma film layers and providing access to functional groups contained therein.

#### 10 Previous Art:

The surfaces of polymeric, metal and ceramic materials are important in many applications. Often these surfaces must be modified for a specific use. For example, surfaces of medical devices implanted in the body must have biocompatible surfaces.

Different methods are generally employed to modify the surfaces of polymers, as opposed to metal and ceramic surfaces. Several conventional methods of surface modification employ wet chemical processes. Most recently developed are energetic methods of surface modification. Each of these methods for each type of material is discussed below.

Wet chemical surface modification of metals and ceramics is accomplished either by forming composites where the metals and ceramics are blended with matrix resin, or by coating these substances with organic coatings.

A typical wet chemical approach of surface modification of polymeric materials employs acids to etch and oxidize the surface. Other approaches employ solvent swelling and penetration of topical coatings into the swollen surfaces. Upon evaporation of the solvent, the coating is incorporated into the top layer of the polymeric article.

There are many problems associated with use of solvents and other wet chemical methods for modifying surfaces. For example, the use of wet chemical methods to modify surfaces can take several steps to accomplish. The chemicals used are often messy, corrosive and toxic to both humans and the environment. There are

In plasma surface modification, the gas employed for modifying the surface of the polymer is introduced into the vacuum chamber containing the surface to be modified. The gas is ionized using RF energy and this ionized gas interacts with the surface of the material. Ionized gases contain a mixture of highly reactive chemical species that include free radicals, electrons, ions and metastable reactive species. These species easily break the chemical bonds on the surface of polymeric materials and substitute the desired chemical groups on the surface of the material. In this manner carbonyl, carboxylic acid, hydroxy, and amine functional groups have been incorporated into and hence become a part of polymeric surfaces.

The design of the reaction chamber, the distribution of power, the excitation frequency, and the gas dynamics are critical factors influencing the properties and efficiency of plasma reactions. Extensive work has been published that shows a direct correlation between excitation frequency and plasma reactivity.

Unlike polymeric materials, metals and ceramics do not contain bonds that can be easily broken. Plasma film deposition offers a means for modifying the surfaces of such materials. In this process monomers consisting of polyatomic molecules are typically ionized using RF energy.

Using plasma polymerization (or plasma film deposition), functional groups can be incorporated into or deposited on any surface, including polymers, metals, ceramics and composites. The films deposited using plasma polymerization are compositionally very different from the polymers formed in bulk processes of polymeric materials using these same monomers. Materials such as methane, propane, and other saturated hydrocarbons are commonly employed to deposit plasma polymerized films on metals and ceramics. Additionally, the film can be comprised of amines, acids, methacrylates, glycidyls or mixtures such as methane and amine, or methane and acid.

When depositing functional films on surfaces using plasma film deposition, the functional density in most cases is limited to that achieved by a monolayer. For example, 11 atom % nitrogen in films deposited from diaminocyclohexane on polystyrene was reported in *Clinical Materials* 11 (1992). This concentration equates

and can be easily abraded away. Furthermore, during plasma film deposition, there are two competing processes that occur. One is the deposition of the film and the other is the ablation of the film being deposited. The degree to which one process predominates is a function of both the process conditions being employed and the chemical nature of the film being deposited. In an attempt to build sufficient functional density on the surface using plasma polymerization, there is also an inherent risk that some of the film being deposited will be ablated away due to the process conditions that need to be employed.

Even if sufficiently long chains of reactive groups could be deposited, the groups at the lower regions of the film may not be as easily accessible for interactions with coating materials as is desired. For example, in films deposited from allylamine, it has been found that a primary amine concentration on the surface is not as high as would be expected from the nitrogen content of the surface measured by ESCA. It has been concluded that perhaps some of these functional groups were buried and not accessible on the surface for reaction with the derivatizing reagents used in their analysis.

Finally, star polymers have been created employing wet chemical methods. For example, the synthesis of star polymers have been reported after reacting multifunctional isocyanates with glycols.

In U. S. Patent Nos. 4,507,466; 4,588,120; 4,568,737; 4,587,329; and 4,694,064, herein incorporated by reference, Tomalia, *et al.* disclose synthesis of giant star polymers commonly referred to as "dendrimers". In the noted patents, sequential reactions of methylacrylate and ethylenediamine are achieved employing methanol as a solvent. Star polymers offer several advantages, namely, a network structure that provides physical strength and the ability to provide high chemical functional densities.

There are several problems associated with star polymers. First, the conventional method of building molecules from the core produces only small quantities of star polymers and requires several days to accomplish. Second, large scale synthetic methods remain to be developed.

### SUMMARY OF THE INVENTION

The present invention substantially reduces or overcomes all of the problems associated with the prior art. The invention provides a novel three-dimensional functional film network and a rapid process for producing same. The employment of  
5 three dimensional film networks with the desired functional groups located either on the periphery or both the periphery and interstitial spaces of the networks of the invention offers a means for significantly increasing the surface functional density in a novel manner. The spatial configuration of the network, and thereby access to the internal structure of the network, is controlled by selecting which functional groups  
10 are sequentially deposited. The novel process of the invention employs sequential radio frequency (RF) deposition, thereby allowing for large scale synthesis. Additionally, no wet chemistry is employed, thereby decreasing production time from days to minutes.

The present invention provides a "forest" or a "mushroom" with many  
15 functional groups on the periphery. The approach has not been previously achieved using plasma deposition and it is not readily obvious or feasible.

In the present invention, sequential deposition is coupled with an infinite variation in the type and functionality of the monomers employed to determine the ultimate structure of the film that is deposited. These variables are employed in  
20 addition to the variation of process conditions to control film structure.

Accordingly, it is an object of this invention to provide a functional film network comprising a plurality of sequentially deposited RF plasma layers.

It is also an object of this invention to provide high functional density film networks with controllable amounts of crosslinking and interstitial spacing, providing  
25 access to the functional groups contained therein.

It is also an object of this invention to provide means for large scale depositions that can be accomplished in a relatively short time.

In accordance with the above objects and those that will be mentioned and will become apparent below, the three-dimensional functional film network in accordance  
30 with this invention comprises a plurality of radio frequency discharge plasma film

and triethylene glycol dimethyl ether; mixtures of the above compounds; and mixtures of a hydrocarbon such as methane or ethylene and the classes of compounds named herein.

Monomer sources of isocyanate functional groups include, but are not limited to, allyl isocyanate, toluene-2,4-diisocyanate, 1,4-diisocyanatobutane, ethyl isocyanate, hexamethylene diisocyanate, toluene-2,6-diisocyanate and mixtures thereof.

Monomer sources of triazine functional groups include, but are not limited to, acrylonitrile, 2,4-diamino-6-methyl-1,3,5-triazine, 1-trimethylsilyl-1,2,4-triazole and mixtures thereof.

Monomer sources for amine functional groups include, but are not limited to, unsaturated amines such as allylamine and vinyl amine; primary amines such as methylamine, butyl amine, propylamine, hydroxyethyl amine and other alkyl amines; alkane diamines such as ethylenediamine, 1,3 diaminopropane, 1,4 diamino butane, 1,5 diamino pentane, 1,6 diamino hexane, 1,7 diamino heptane, 1,8 diamino octane; polyalkylene polyamines such as diethylenetriamine, dipropylene triamine, dibutylenetriamine, triethylenetetramine, tripropylenetetramine, tributylenetetramine, N, N'-bis(2-aminoethyl)-1,3-propanediamine, bis(3-aminopropyl)amine; aminosilanes such as 3-Aminopropyltrimethoxysilane, 3-Aminopropyltriethoxysilane, 3-Aminopropylmethyldiethoxysilane, 3-(3-Aminophenoxy)propyltrimethoxysilane, 3-(2-Aminoethylamino)propyltrimethoxysilane, hexamethyldisilazane, and other similar compounds; heterocyclic amines such as ethylene amine, piperidines, pyrroles and pyrrolidines; aromatic amines such as aniline; and various other amines and amino compounds such as mercaptoethylamine, acrylonitrile, acetonitrile, butyronitrile, and 1,4 diaminocyclohexane; mixtures of the above compounds; and mixtures of a hydrocarbon such as methane or ethylene and the classes of amino compounds named herein.

Monomer sources for carboxylic acid functional groups include, but are not limited to, oxygen, carbon dioxide and compounds such as acetic acid, propionic acid, butyric acid, 2-methyl propionic acid, n-pentanoic acid, 4-methyl butanoic acid,

having amine is reacted with monomers that will deposit ethylene functional groups, producing two network branches in the new layer of the network.

TABLE I

Reactive Pairs that Initiate Extended Chains

	Surface or Chain-End Function	Reacts With	To Produce
1.	$-\text{NH}_2$	$\text{CH}_2=\text{CHX}$	$-\text{N} \begin{cases} \text{CH}_2\text{CH}_2\text{X} \\ \text{CH}_2\text{CH}_2\text{X} \end{cases}$
2.	$-\text{NH}_2$	$\text{O}=\text{C} \begin{cases} \text{R}_1 \\ \text{R}_2 \end{cases}$	$-\text{N}=\text{C} \begin{cases} \text{R}_1 \\ \text{R}_2 \end{cases}$
3.	$-\text{COOH}$	$\text{NH}_2\text{R}$	$-\text{CONHR}$
4.	$-\text{COOH}$	$\text{NHR}_1 \begin{smallmatrix} \diagdown \\ \text{R}_2 \end{smallmatrix}$	$-\text{CO}-\text{N} \begin{smallmatrix} \diagup \text{R}_1 \\ \diagdown \text{R}_2 \end{smallmatrix}$
5.	$-\text{COOH}$	$\text{NH}_2(\text{CH}_2)_n\text{NH}_2$	$-\text{CONH}(\text{CH}_2)_n\text{NH}_2$
6.	$-\text{COOR}$	$\text{NH}_2\text{R}$	$-\text{CONHR}$
7.	$-\text{COOR}$	$\text{NHR}_1 \begin{smallmatrix} \diagdown \\ \text{R}_2 \end{smallmatrix}$	$-\text{CO}-\text{N} \begin{smallmatrix} \diagup \text{R}_1 \\ \diagdown \text{R}_2 \end{smallmatrix}$
8.	$-\text{COOR}$	$\text{NH}_2(\text{CH}_2)_n\text{NH}_2$	$-\text{CONH}(\text{CH}_2)_n\text{NH}_2$
9.	$-\text{CHO}$	$\text{NH}_2\text{R}$	$-\text{CH}=\text{NR}$
10.	$-\text{NCO}$	$\text{NH}_3$	$-\text{NHCONH}_2$
11.	$-\text{NCO}$	$\text{NH}_2\text{R}$	$-\text{NHCONHR}$
12.	$-\text{NCO}$	$\text{NHR}_1 \begin{smallmatrix} \diagdown \\ \text{R}_2 \end{smallmatrix}$	$-\text{NHCO}-\text{N} \begin{smallmatrix} \diagup \text{R}_1 \\ \diagdown \text{R}_2 \end{smallmatrix}$
13.	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \cdots \text{CH}_2 \end{array}$	$\text{RNH}_2$	$\begin{array}{c} \text{OH} \\ \diagup \\ \text{CH} \cdots \text{CH}_2\text{NHR} \end{array}$
14.	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \cdots \text{CH}_2 \end{array}$	$\text{NHR}_1 \begin{smallmatrix} \diagdown \\ \text{R}_2 \end{smallmatrix}$	$\begin{array}{c} \text{OH} \\ \diagup \\ \text{CH} \cdots \text{CH}_2\text{N} \begin{smallmatrix} \diagup \text{R}_1 \\ \diagdown \text{R}_2 \end{smallmatrix} \end{array}$



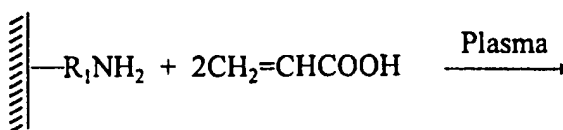
According to a preferred embodiment of the invention, the construction of the film network occurs as follows: an initial plasma polymerized film layer is first deposited on the substrate. This initial layer can be chosen from the class of compounds such as ammonia, unsaturated amines, primary amines, aliphatic  
5 diamines, polyalkylene polyamines, heterocyclic amines, nitriles, pyrroles, pyrrolidines, aminosilanes and mixtures thereof such that an amine functional group is formed on the surface. The initial layer may also comprise oxygen, water, carbon dioxide, and mixtures of a hydrocarbon and the above referenced compounds. The second plasma deposited layer is applied using the class of compounds consisting of;  
10 (i) saturated carboxylic acids such as acetic acid, propionic acid, butyric acid, 2-methyl propionic acid, n-pentanoic acid, 4-methyl butanoic acid, n-hexanoic acid, and unsaturated carboxylic acids such as acrylic acid, methacrylic acid and similar unsaturated acids; or (ii) esters such as methyl acrylate, methylmethacrylate, glycidyl methacrylate and similar class of compounds; or (iii) keto esters such as carbonyl-bis-  
15 3,3'-methyl propionate and similar compounds; or (iv) oxygen and carbon dioxide (v) mixtures of hydrocarbons and the class of compounds named in groups (i) through (iv). The second layer can also be constructed by using monomers that consist of a mixture of compounds chosen from groups (i) and (ii). Of the three classes of compounds mentioned, it is preferred that the monomer for the second layer  
20 be chosen from the class of compounds described in groups (i) and (ii).

The plasma deposited film network can also be initiated by depositing a film using the monomers from the class of compounds consisting of; (i) saturated carboxylic acids such as acetic acid, propionic acid, butyric acid, 2-methyl propionic acid, n-pentanoic acid, 4-methyl butanoic acid, n-hexanoic acid, and unsaturated  
25 carboxylic acids such as acrylic acid, methacrylic acid, and other similar materials; or (ii) esters such as methyl acrylate, methyl methacrylate, glycidyl methacrylate and other similar materials; or (iii) oxygen and carbon dioxide; or (iv) mixtures of hydrocarbons and the class of compounds named in groups (i) through (iii). This first layer can also be formed from a mixture of monomers described in groups (i), (ii) and  
30 (iv) or the mixtures described in group (v). The second layer of plasma polymerized

acid is shown. The two hydrogen bonds on each amine are easily broken. The process can be adjusted so that there is more than one carboxylic acid deposited. For example, if pulse plasma is employed as illustrated in Step 2 below, two carboxylic acid units will attach at the nitrogen, creating two branches.

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## STEP 2

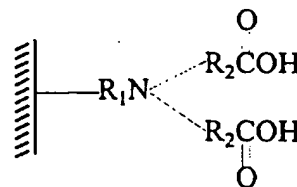


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Formula 2

Formula 3

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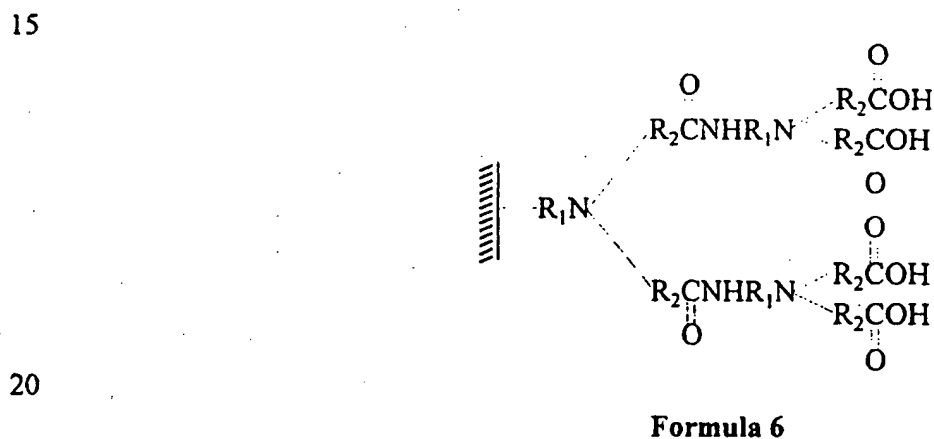
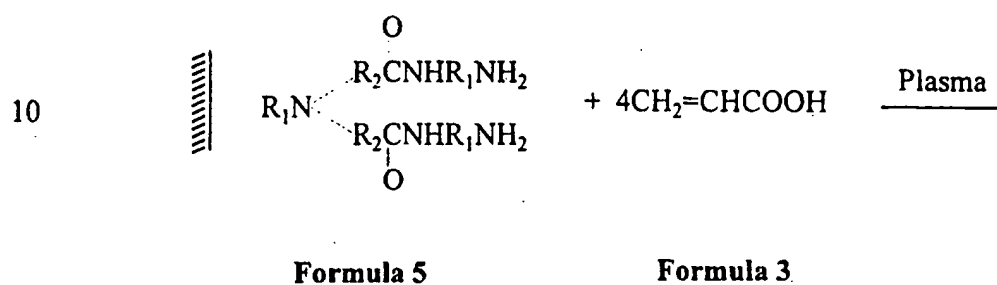


Formula 4

The purpose of Step 3 is to provide another point for branching. For example, as illustrated below, an ethylene diamine plasma is again employed. Reacting these amines with the carboxylic acid functional groups deposited in Step 2 provides amides. At the other end of each amide is an amine which provides another opportunity to provide two branches.

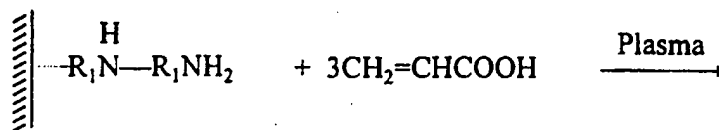
two hydrogen bonds on each amine are again easily broken, as previously shown in Step 2. The process can be adjusted so that there is more than one carboxylic acid deposited. For example, if pulse plasma is employed as illustrated in Step 4 below, two more carboxylic acid units will attach at the nitrogen, providing four branches for each amine functional group attached to the surface.

## STEP 4



molecule can occur in a plasma at the location shown by the dotted line. In a manner analogous to deposition from a diamine, and as shown below, a surface with three attachment points can be obtained, one at the secondary amine and two at the primary amine site.

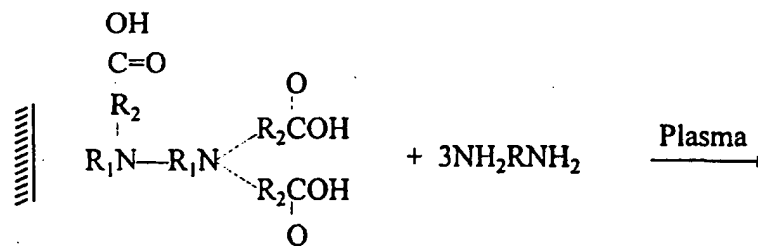
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Formula 8

Formula 3

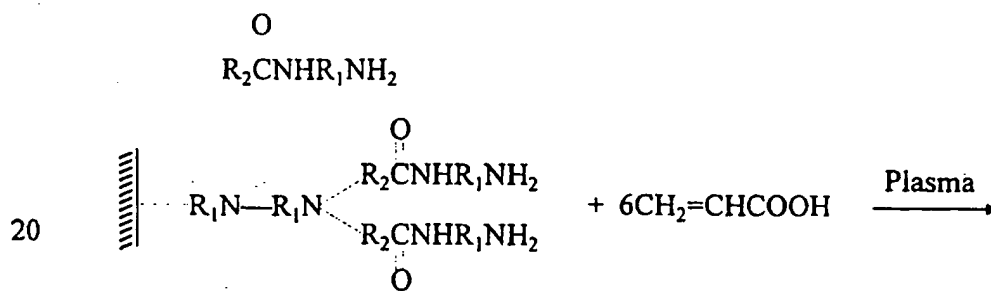
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Formula 9

Formula 1

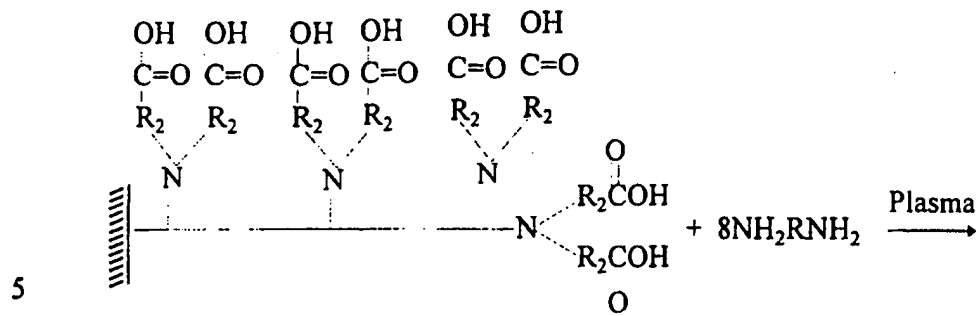
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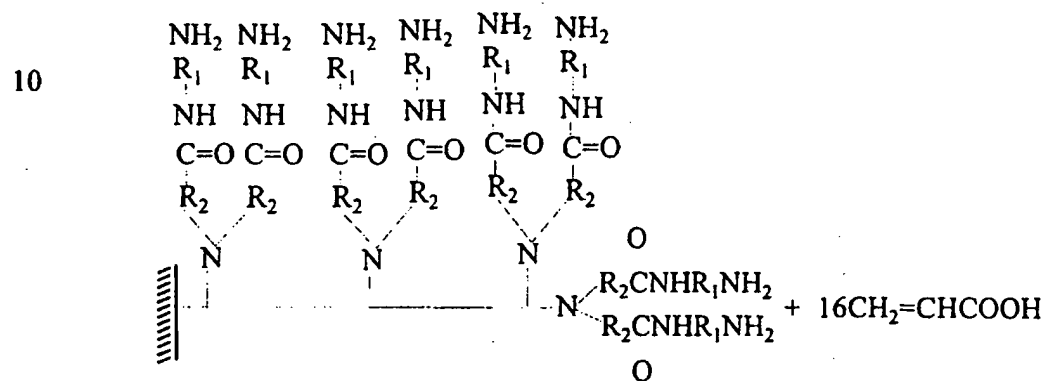
Formula 10

Formula 3



Formula 13

Formula 1



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Formula 14

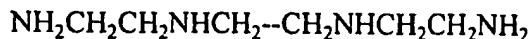
Formula 3

In Step 2, an acid monomer may be employed such as acrylic acid, methacrylic acid, propionic acid, and hexanoic acid. Another class of monomers that can be employed within the scope of the invention, as illustrated in Step 2, are the acrylates. Monomers of this class include but are not limited to methyl acrylate and methylmethacrylate. The hydrocarbon end of the acid or acrylate is substituted for each hydrogen on the amine to form an amide.

The applicants have found that monomers with higher numbers of carbons in their backbone will result in a network structure having a loose network, thereby increasing interstitial spacing between plasma film layers, while those with shorter carbon chains will result in tighter networks.

Additionally, the applicants have found that when using monomers with more than two functional groups, a much higher level of branching can be obtained thereby controlling the network structure. The following examples according to the invention illustrate the employment of different functional densities and different backbone chain lengths to provide a network structure having a loose network, thereby increasing interstitial spacing between plasma film layers as compared to other films for providing access to the functional groups contained therein.

The film network construction can, as an example, be started with a deposition using triethylenetriamine as the monomer. This monomer can be cleaved at the centrally located  $\text{CH}_2 - \text{CH}_2$  bond shown as a dotted line in Formula 16 below.

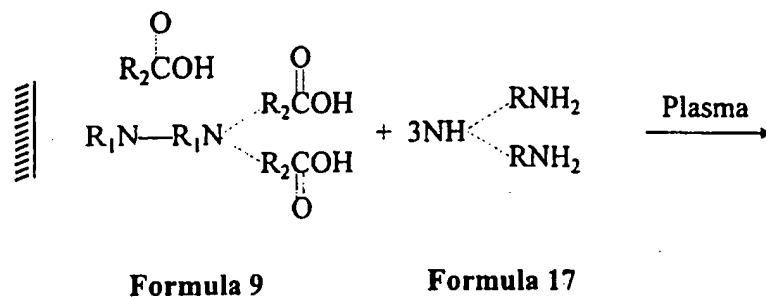


**Formula 16**

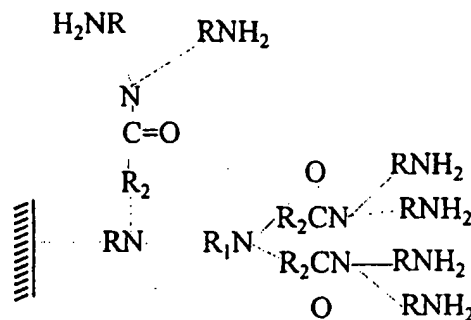
The substrate surface resulting from a plasma deposition using triethylenetriamine is shown below in Formula 8.

At this stage several options are available. Formula 9 can be reacted with Formula 1 to yield Formula 10 or Formula 9 could be reacted with a trifunctional amine, such as diethylenetriamine, represented by Formula 17 below, to yield Formula 18.

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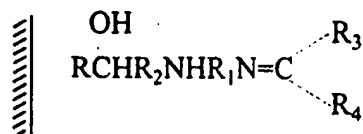
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Formula 18

The chemical functional group density of Formula 18 is much different than the chemical functional group density of Formula 10, which was also derived from Formula 9. Thus by mixing and matching the reactive functionality ("monofunctional," "difunctional," "trifunctional" etc.) of the monomer employed, plasma deposited film networks with different morphologies and densities can be provided. Although multifunctional amines and acrylic acid have been employed to illustrate the construction of the plasma deposited film network, it will be apparent to those skilled in the art that the starting film can be constructed from any of the monomers described earlier and combined with the appropriate reactive pair shown in the second column of Table I.



Formula 23

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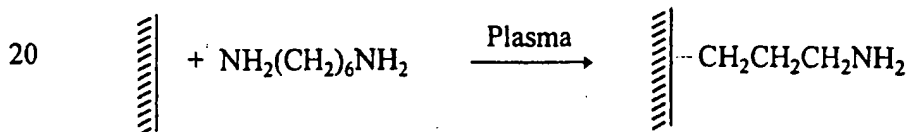
$R_3$  and  $R_4$  can be any aliphatic or aromatic groups, aliphatic groups being preferred.  $R_3$  and  $R_4$  can include a reactive chemical functional group and these sites can be employed to continue to build the film network. Thus the construction of the plasma deposited film network can be accomplished by using the appropriate reactive

10 pairs described in Table I without limitation.

When a network having a open network (i.e., increased interstitial spacing between plasma film layers) is desired, monomers can be chosen such that the central chain can be represented by the notation  $(\text{CH}_2)_n$  where "n" is sufficiently large. As illustrated below, when the value of six (6) is chosen for "n" in the amine, represented

15 by Formula 24, and a value of two (2) is chosen for "n" in the allylic acid monomer, Formula 26, allyl acetic acid, Formula 28 in Step 2, results.

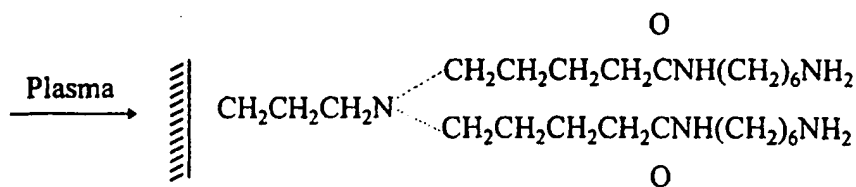
## STEP 1



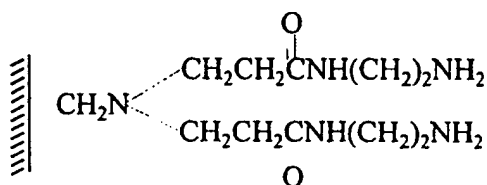
Formula 24

Formula 25



**Formula 28**

- 5 As the structure shown in Formula 28 illustrates, the film network of the present invention has a loose network, thereby increasing interstitial spacing between plasma film layers as compared to the crosslink density and interstitial spacing obtained when ethylene diamine and acrylic acid are reacted using the same three steps illustrated by Formula 29. It will be apparent to those skilled in the art that by
- 10 using monomers with different central chain lengths and different reactive functionalities, the morphology and the chemical group functionality of the plasma deposited film network can be adjusted in many ways.



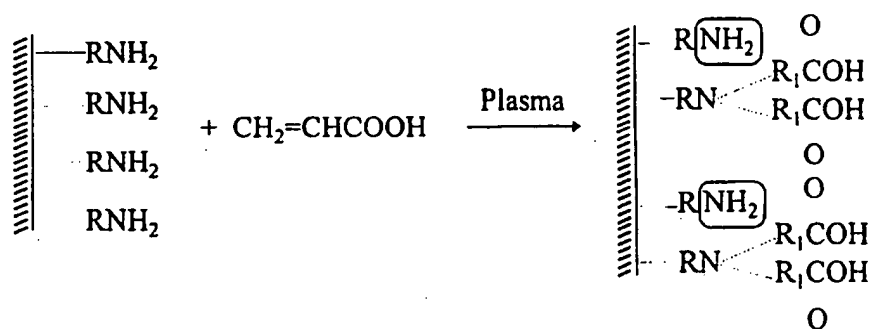
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**Formula 29**

acid deposition process is adjusted such that only part of the amines react, two objectives are accomplished. One is that a network structure having an open network, thereby increasing interstitial spacing between plasma film layers as compared to other films is provided. The other is that some reactive functional groups inside the network structure are retained rather than having all functional groups on the periphery.

According to the invention, a method for preventing reaction of all functional groups employs short deposition times, which only partially covers the previously deposited film. Another method for controlling the crosslink density and interstitial spacing of the network structure and retaining functional reactivity inside the network is shown in Formulas 34-37 below. Here, process conditions are selected such that not all of the functional sites would become growth sites.

For example, by the decreasing the deposition time in the second step of the process, which in the example is the deposition of acrylic acid, from the 2 minute normal process time to 30 seconds, many of the amine functional groups deposited in the first layer are left unreacted. Another method of reducing the reaction between the amine in the first layer and the acrylic acid being deposited is to reduce the flow of acrylic acid while maintaining the same process time. As shown in Formula 35 below, if not all functional sites become growth sites, some reactive functional groups remain within the interstices of the network (shown circled).

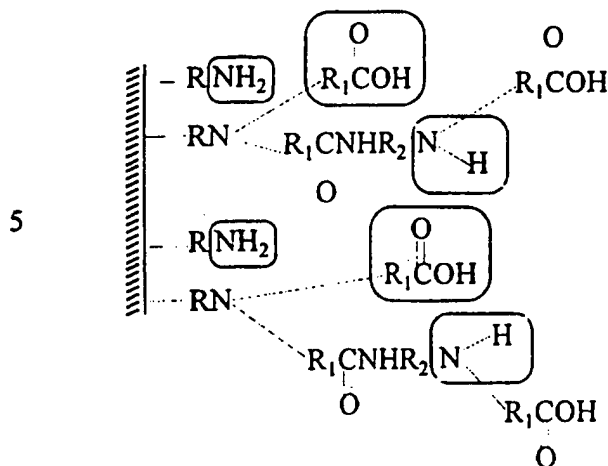


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Formula 34

Formula 3

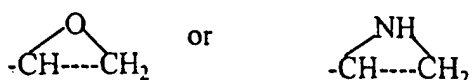
Formula 35



Formula 37

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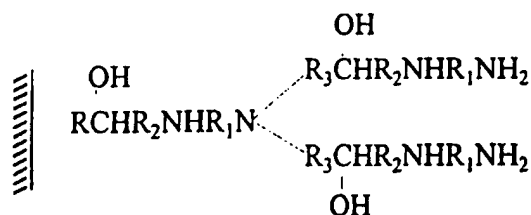
Another method for achieving a plasma deposited film network with chemical functional group in the interstices of the film can be illustrated by the following process scheme. In this case monomers with the epoxy functional group such as



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are employed. Once the three-membered ring is opened in the second step, during deposition of an amine, the epoxy group leaves behind a chemical functional group. For example, as previously shown in Formula 19, glycidyl methacrylate could be employed in the first deposition step of the network construction process to yield a surface with the epoxy reactive group, Formula 20, (often referred to as the oxirane group). As shown in Formulas 20-39 below, this surface with the epoxy reactive group, Formula 20, can now be reacted with an amine, for example, Formula 1, and as suggested in Table I to yield Formula 21 below. As Formula 21 illustrates, we are left with a hydroxyl group near the surface and an amine as a terminal group. Formula 21

20



Formula 39

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In this manner hydroxy chemical groups can be incorporated in the interstices of the plasma deposited film network while the peripheral chemical groups can be of an entirely different category, such as an amine, by the choice of the monomer employed in the termination step of the deposition process.

10

Another method for creating chemical functional groups in the interstices of the plasma deposited film network would follow the scheme illustrated in Formulas 1-41 below. In this process, the network construction is initiated with the deposition of an amine, Formula 1, which is then reacted with a ketone, Formula 40, where the ketone group is located such that the chemical groups on either side of the ketone group are of differing length and are terminated with a chemical functional group.

15

When this ketone is now reacted with another monomer (not shown), the longer arm will react more easily, whereas the shorter arm may become protected by steric hindrance, thereby remaining intact within the film structure.

A manual throttle valve was employed to control the reaction chamber pressure independent of the monomer flow.

Step 1: Plasma polymerization of ethylene diamine.

Ethylene diamine is fed to the reaction chamber by evaporating ethylene diamine contained in an Erlenmeyer flask that is maintained at 30°C. The plasma polymerization is conducted at a power setting of 90 watts and a reaction chamber pressure of 420 mTorr. The flow and therefore the residence time of the monomer in the reaction chamber is controlled by the throttle valve. The throttle valve is adjusted so that the actual pressure in the reaction chamber is 480 mTorr. The process time is 3 minutes. These films are deposited on 120µm polystyrene beads. Chemical analysis using a ninhydrin test for primary amines shows a concentration of 1.1 µmole/gm. The surface area of these beads is 476 cm<sup>2</sup>/gm. The amine concentration measured equates to a surface concentration of 4 nmoles/cm<sup>2</sup>. This surface density is equivalent to a monolayer of functional groups on the surface.

Step 2: Plasma polymerization of acrylic acid.

In this step, an acrylic acid plasma polymerized film is deposited on top of the amine film deposited in Step 1. The acrylic acid is fed to the reactor by bubbling helium through the monomer contained in an Erlenmeyer flask. The power is set at 100 watts, the helium flow rate is 15 cc/min and the pressure is 500 mTorr. The acrylic acid is maintained in a water bath whose temperature is controlled to 45° C. The flow and therefore the residence time of the monomer in the reaction chamber is controlled by the throttle valve. The throttle valve is adjusted so that the actual pressure in the reaction chamber is 580 mTorr. The plasma is pulsed at 10 Hz and a 10% duty cycle is employed. Deposition of acrylic acid on untreated 180 µm polystyrene beads under these conditions and a process time of 4 minutes results in a functional density of 2.1 µmol acid groups/gm. This functional density translates to 6.8 nmoles/cm<sup>2</sup>. Since we already have approximately 2.3 nmoles/cm<sup>2</sup> of amines on the surface and each amine group can add two acrylic acid groups, the process time for this step is 3 minutes. It is assumed that the functional density previously

**CLAIMS**

What is claimed is:

1. A three dimensional film network, comprising:  
a plurality of radio frequency discharge plasma film layers, said  
5 plasma film layers including a first layer and a second layer disposed immediately  
adjacent said first layer;  
said first layer including a plurality of a first functional group;  
and  
said second layer including a plurality of a second functional  
10 group.
2. The three dimensional film network according to Claim 1 including  
interstitial spaces disposed within said network which provides access to said film  
layers.
3. The three dimensional film network according to Claim 1 wherein, said  
15 first and said second layers are at least partially covalently bonded.
4. The three dimensional film network according to Claim 1 wherein, said  
first functional group comprises an amine functional group.
5. The three dimensional film network according to Claim 1 wherein, said  
second functional group is selected from the group consisting of carboxy, carboxylic  
20 ester, epoxy, isocyanate, hydroxy and sulfhydryl.
6. The three dimensional film network according to Claim 1 wherein, said  
first functional group is selected from the group consisting of carboxy, carboxylic  
ester, epoxy, amine, isocyanate, hydroxy and sulfhydryl.
7. The three dimensional film network according to Claim 1 wherein, said  
25 second functional group is selected from the group consisting of carboxy, carboxylic  
ester, epoxy, amine, isocyanate, hydroxy and sulfhydryl.
8. The three dimensional film network according to Claim 7 wherein, said  
second functional group is reactive with said first functional group.

17. The three dimensional film network according to Claim 15 wherein, said first and said second layers are at least partially covalently bonded.

18. The three dimensional film network according to Claim 15 wherein, said first functional group comprises an amine functional group.

5 19. The three dimensional film network according to Claim 15 wherein, said second functional group is selected from the group consisting of carboxy, carboxylic ester, epoxy, isocyanate, hydroxy and sulfhydryl.

20. The three dimensional film network according to Claim 15 wherein, said first functional group is selected from the group consisting of carboxy, carboxylic ester, epoxy, amine, isocyanate, hydroxy and sulfhydryl.

21. The three dimensional film network according to Claim 15 wherein, said second functional group is selected from the group consisting of carboxy, carboxylic ester, epoxy, amine, isocyanate, hydroxy and sulfhydryl.

22. The three dimensional film network according to Claim 21 wherein, 15 said second functional group is reactive with said first functional group.

23. The three dimensional film network according to Claim 15 wherein, said film network includes a dual branched spatial configuration between said adjacent film layers.

24. The three dimensional film network according to Claim 15 wherein, 20 said three dimensional network includes a triple branched spatial configuration between said adjacent film layers.

25. The three dimensional film network according to Claim 15 wherein, said three dimensional film network includes a quadruple branched spatial configuration between said adjacent film layers.

25 26. The three dimensional film network according to Claim 15 wherein, said three dimensional film network includes a heterocyclic ring spatial configuration between said adjacent film layers.

36. The substrate structure according to Claim 35 wherein, said second functional group is reactive with said first functional group.

37. The substrate structure according to Claim 29 wherein, said substrate structure includes a dual branched spatial configuration between said adjacent film  
5 layers.

38. The substrate structure according to Claim 29 wherein, said substrate structure includes a triple branched spatial configuration between said adjacent film layers.

39. The substrate structure according to Claim 29 wherein, said substrate  
10 structure includes a quadruple branched spatial configuration between said adjacent film layers.

40. The substrate structure according to Claim 29 wherein, said substrate structure includes a heterocyclic ring spatial configuration between said adjacent film layers.

41. The substrate structure according to Claim 29 wherein, said substrate  
15 structure includes a linear chain spatial configuration between said adjacent film layers.

42. The substrate structure according to Claim 41 wherein, said linear chain includes a plurality of a third functional group selected from the group  
20 consisting of carboxy, carboxylic ester, epoxy, amine, isocyanate, hydroxy and sulfhydryl.

43. A method for sequentially depositing a three-dimensional functional film network on a substrate, comprising the steps:

positioning a substrate having a surface thereon in a radio  
25 frequency plasma discharge apparatus;

inserting into said radio frequency plasma discharge apparatus a first plasma medium, said first plasma medium comprising a first compound selected from the group consisting of ammonia, unsaturated amine, primary amine, aliphatic diamine, polyalkylene polyamine, aminosilane, heterocyclic amine, nitrile, pyrrole,



51. The method according to Claim 43 wherein, said second plasma medium comprises water.

52. The method according to Claim 43 wherein, said second plasma medium comprises a mixture of a hydrocarbon and said first compound.

5 53. The method according to Claim 43 wherein, said first plasma medium comprises a third compound selected from the group consisting of ammonia, unsaturated amine, primary amine, aliphatic diamine, polyalkylene polyamine, aminosilane, heterocyclic amine, nitrile, pyrrole, pyrrolidine and mixtures thereof.

54. The method according to Claim 43 wherein, said first plasma medium  
10 comprises a mixture of a hydrocarbon and said third compound.

55. The method according to Claim 53 wherein, said first functional group comprises an amine functional group.

56. The method according to Claim 55 wherein, said second plasma medium comprises a fourth compound selected from the group consisting of saturated  
15 carboxylic acid, unsaturated carboxylic acid, carboxylic ester, keto ester and mixtures thereof.

57. The method according to Claim 56 wherein, said second plasma medium comprises a mixture of a hydrocarbon and said fourth compound.

58. The method according to Claim 55 wherein, said second plasma  
20 medium comprises oxygen.

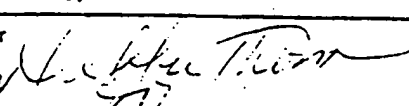
59. The method according to Claim 56 wherein, said second functional group is selected from the group consisting of carboxy, carboxylic ester, epoxy, isocyanate, hydroxy and sulfhydryl.

60. The method according to Claim 43 wherein, said first functional group  
25 is selected from the group consisting of carboxy, carboxylic ester, epoxy, amine, isocyanate, hydroxy and sulfhydryl.

61. The method according to Claim 43 wherein, said second functional group is selected from the group consisting of carboxy, carboxylic ester, epoxy, amine, isocyanate, hydroxy and sulfhydryl.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/20267

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) : C08F 2/48; C23C 14/28, 14/30; H05B 6/00; H05H 1/02, 1/24. US CL : Please See Extra Sheet. According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 427/488, 508, 569, 570, 595; 428/420, 423.1, 423.5, 424.7, 474.4, 474.7, 475.2, 520, 522. Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,693,799 A (YANAGIHARA ET AL) 15 September 1987, col. 1, lines 56-64; col. 4, lines 42-59; col. 5, line 52 to col. 6, line 5; col. 6, lines 16-25; and col. 7, lines 9-30.	1--3, 9-13, 15-17, 23-27, 29-32, 37-41, and 43-68.
A	US 4,587,329 A (TOMALIA et al) 06 May 1986, entire document	1-68
A	US 5,342,693 A (WINTERS et al) 30 August 1994, entire document.	1-68
A	US 5,449,383 A (CHATELIER et al) 12 September 1995, entire document.	1-68
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
*A*	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*E*	earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*L*	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O*	document referring to an oral disclosure, use, exhibition or other means	*G* document member of the same patent family
*P*	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search 17 MARCH 1997		Date of mailing of the international search report 19 MAY 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer HOA THI LE  Telephone No. 703-308-2415

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## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

427/488, 508, 569, 570, 595;

428/420, 423.1, 423.5, 424.7, 474.4, 474.7, 475.2, 520, 522.